

Effect of Ca substitution and pressure on the transport and magnetic properties of $\text{Sr}_{14}\text{Cu}_{24}\text{O}_{41}$ with doped two-leg Cu-O ladders

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Anisotropic electrical resistivity and magnetic susceptibility are measured on single crystals of $\text{Sr}_{14-x}\text{A}_x\text{Cu}_{24}\text{O}_{41}$ ($A = \text{Ca}, \text{Y}$). This material contains two-leg antiferromagnetic spin ladders that are progressively doped with hole carriers upon Ca substitution and thus determine the charge-transport properties. Application of hydrostatic pressure to this system has an effect similar to Ca substitution, increasing the hole density in the ladders. The resistivity shows remarkable anisotropy, indicative of a one-dimensional electronic state. [S0163-1829(97)51406-8]

After high-temperature superconductivity was discovered¹ in doped two-dimensional (2D) antiferromagnetic (AF) copper oxides, one-dimensional (1D) cuprates with the same Cu-O bonds have attracted much interest. Particularly, ladders with an even number of coupled Cu-O chains are predicted to have a finite spin gap reminiscent of that in the underdoped high- T_c cuprates, and the theoretical works suggest a possibility of superconductivity when doped with holes.^{2,3} To understand the electronic state of such quasi-1D systems the measurements using single crystals are indispensable. We present here the results of electrical resistivity and magnetic susceptibility measured on single crystals of the $\text{Sr}_{14}\text{Cu}_{24}\text{O}_{41}$ system which contains two-leg Cu-O ladders. The anisotropy indicates that the electronic state of this system is really one-dimensional. The holes are localized in the chains, another structural unit of $\text{Sr}_{14}\text{Cu}_{24}\text{O}_{41}$, and are transferred to ladders upon Ca substitution for Sr, where they become mobile and would possibly superconduct under some conditions.⁴

The experimental studies on the two-leg ladder system so far have been performed on undoped SrCu_2O_3 (Ref. 5) and doped $(\text{La}, \text{Sr})\text{CuO}_{2.5}$.⁶ Although the structure of these compounds are simple, they can be synthesized only under high pressure. To the contrary, $\text{Sr}_{14-x}\text{A}_x\text{Cu}_{24}\text{O}_{41}$ ($A = \text{Ca}, \text{Y}$) can be synthesized under ambient pressure. Because of this, many studies have recently been done.^{4,7-13} The structure of $\text{Sr}_{14}\text{Cu}_{24}\text{O}_{41}$ is not simple. It consists of an alternating stack of the plane containing two-leg Cu_2O_3 ladders, and the plane containing edge-sharing CuO_2 chains [shown in the inset of Fig. 1(a)] sandwiched by Sr layers.^{14,15} The average valence of $\text{Sr}_{14}\text{Cu}_{24}\text{O}_{41}$ is +2.25, but the resistivity shows semiconducting behavior,⁸⁻¹¹ suggesting that the hole carriers are not effectively doped into the conducting path. Isovalent Ca substitution for Sr remarkably reduces the resistivity,⁸⁻¹⁰ although the average Cu valence does not change. The average valence decreases upon Y substitution, making the compound more insulating. The compound in which the valence of Cu in both chain and ladder sites is +2, can also be synthesized as $\text{La}_6\text{Ca}_8\text{Cu}_{24}\text{O}_{41}$.¹⁵ So far, most measurements have been performed using polycrystalline samples, so that they lack the information on the anisotropy and the contribution from each structural unit is not clear.

In this study, we prepared single crystals with various compositions, $\text{Sr}_{14}\text{Cu}_{24}\text{O}_{41}$, $\text{Sr}_{14-x}\text{Ca}_x\text{Cu}_{24}\text{O}_{41}$ ($x = 1, 3, 6, 11$), $\text{Sr}_{14-x}\text{Y}_x\text{Cu}_{24}\text{O}_{41}$ ($x = 1, 3$), and $\text{La}_6\text{Ca}_8\text{Cu}_{24}\text{O}_{41}$. They were grown by the traveling-solvent-floating-zone (TSFZ) method which was successful in growing single crystals of high- T_c cuprates.¹⁶ The growth was done using an infrared furnace under oxygen gas at 3–10 atm. Thus obtained single crystals have typically about 4 mm diam and 50 mm length. These single crystals were characterized using an

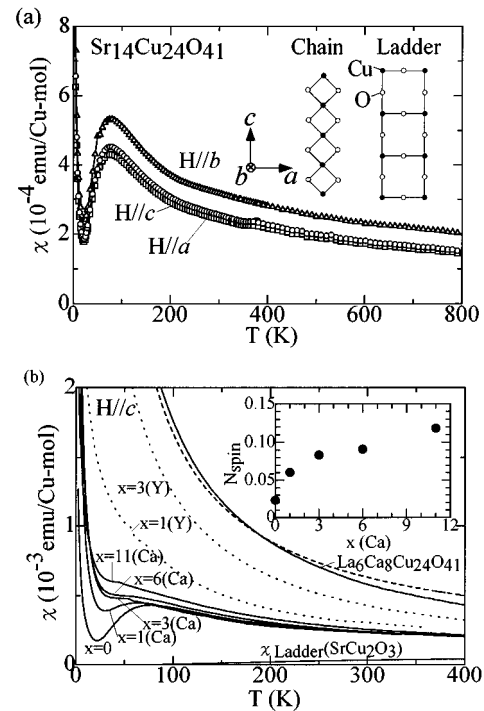


FIG. 1. (a) The temperature dependence of the magnetic susceptibility of $\text{Sr}_{14}\text{Cu}_{24}\text{O}_{41}$ with magnetic field applied along the three axes. (b) The temperature dependence of the susceptibility of $\text{Sr}_{14-x}\text{Ca}_x\text{Cu}_{24}\text{O}_{41}$, $\text{Sr}_{14-x}\text{Y}_x\text{Cu}_{24}\text{O}_{41}$ (dotted curves), and $\text{La}_6\text{Ca}_8\text{Cu}_{24}\text{O}_{41}$ for $H\parallel c$. The dashed line is the expected Curie paramagnetism when all spins on the chain Cu sites are free. The inset shows the Ca content dependence of the number (N_{spin}) of free $S = 1/2$ spins per chain-Cu estimated from the low-temperature Curie term.

x-ray diffractometer and found to be composed of a single domain. The magnetic susceptibility measurements were done using a superconducting quantum interference device (SQUID) dc magnetometer between 2 and 800 K. Above 400 K, we used an oven attachment equipped with the SQUID. The resistivity measurements were performed by a six-probe method in order to confirm there were no defects in the sample. Dots of silver paste were heated as electrodes on the samples at 300 °C in oxygen. The resistivity measurements under high pressure were carried out by using a piston cylinder up to 2 GPa.

In Fig. 1(a), the magnetic susceptibility of $\text{Sr}_{14}\text{Cu}_{24}\text{O}_{41}$ with magnetic field applied along the three principal axes is shown. A characteristic feature of the temperature dependence of susceptibility is a broad peak and a subsequent drop at low temperatures. The susceptibility drop is isotropic, and can be ascribed to the formation of a gap with magnitude of about 130 K in the spin excitation spectrum. This spin gap is considered to be a phenomenon on the CuO_2 chains.^{10,12} Theoretically, the two-leg ladder is expected also to have a spin gap $\Delta_{\text{SG}} \sim J/2$ (J the exchange interaction between neighboring Cu in a ladder).¹⁷ In the Cu_2O_3 ladders, J is considered to be 1000 K or higher.¹⁸ In fact, a large spin gap of ~ 500 K is detected by NMR studies.¹³ With a spin gap of ~ 500 K in the ladders which is similar in magnitude to that in SrCu_2O_3 , the expected susceptibility is indicated by the thin line in Fig. 1. Thus it is reasonable to assume that spins on the ladders have a minor contribution to the susceptibility.

As shown in Fig. 1(b), the temperature dependences of magnetic susceptibility show a significant change upon Ca and Y substitution. This behavior can be explained by the change in the Cu valence in the CuO_2 chain. In $\text{La}_6\text{Ca}_8\text{Cu}_{24}\text{O}_{41}$, the magnetic susceptibility is dominated by a Curie term, the magnitude of which can quantitatively be explained if all the chain Cu^{2+} ions have $S = 1/2$ paramagnetic spins¹⁰ [Fig. 1(b)]. Actually, instead of a gap feature, a feature corresponding to a three-dimensional ordered state is observed below ~ 12 K. A similar situation is also realized in the Y-substituted compounds. In $\text{Sr}_{14}\text{Cu}_{24}\text{O}_{41}$, the susceptibility shows a gap feature at low temperatures. Recent neutron scattering of $\text{Sr}_{14}\text{Cu}_{24}\text{O}_{41}$ gives evidence for a dimerized state between spins separated by two and four times the distance between the nearest-neighbor Cu ions.¹² From this, it is speculated that the number of Cu^{2+} and Cu^{3+} would be nearly equal, and that the spin gap arises from dimerization of two Cu^{2+} ions separated by nonmagnetic Cu^{3+} ion(s), i.e., the alternating Cu^{2+} and Cu^{3+} order along the chain.^{10,12} Then, the Cu valence in the chain is presumably +2.5, and consequently the valence of the ladder Cu is estimated to be $\sim +2.07$.

With increasing Ca, the gap feature becomes gradually smeared because of a progressive development of a Curie term at low temperatures. This Curie term is considered to be due to the free spins not participating in the dimerized state forming Cu^{2+} - Cu^{3+} ordering. The estimated number of free spins is shown in the inset of Fig. 1(b) as a function of Ca content x . The development of a Curie term is explained by the deviation of the chain-Cu valence from +2.5 due to a redistribution of holes between chains and ladders upon Ca substitution. This scenario is in contrast to that proposed by

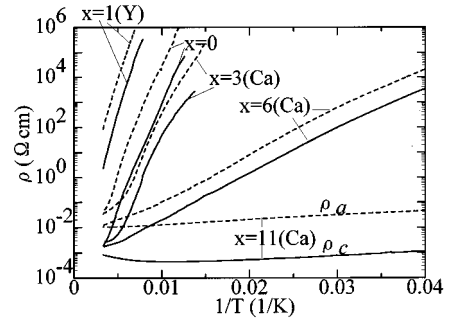


FIG. 2. The Arrhenius plots of the resistivity for $\text{Sr}_{14-x}\text{Ca}_x\text{Cu}_{24}\text{O}_{41}$ and $\text{Sr}_{13}\text{YCu}_{24}\text{O}_{41}$ along the c and a axis (solid and dashed curves, respectively).

Carter *et al.*, who assumed that the Cu valence in the chain does not change with Ca substitution, and that the ladders remain undoped.¹⁰

In Fig. 2, $\ln\rho$ vs $1/T$ plots are shown for the resistivity along the c (parallel to the ladders within the ladder planes) and a axis (perpendicular to the ladders within the ladder planes). All the compounds except for $\text{Sr}_3\text{Ca}_{11}\text{Cu}_{24}\text{O}_{41}$ show a rapid increase in resistivity upon cooling. The value of a -axis resistivity (ρ_a) is by one to two orders of magnitude larger than the c -axis resistivity (ρ_c). The anisotropic ratio, ρ_a/ρ_c , is not strongly dependent on x . While the resistivity becomes larger and the compound becomes more insulating for Y substitution, the Ca substitution makes the compound more conductive.

One should note that $\text{Sr}_{14}\text{Cu}_{24}\text{O}_{41}$ is not highly insulating as compared with the Y-substituted compounds, suggesting that $\text{Sr}_{14}\text{Cu}_{24}\text{O}_{41}$ is slightly doped with carriers. In fact, the reflectivity spectrum with c -axis polarization shows a plasma edge at ~ 0.6 eV, whereas the spectrum of $\text{Sr}_{11}\text{Y}_3\text{Cu}_{24}\text{O}_{41}$ is typical of an insulator.¹⁹ The plasma edge at such low energy arises from charge carriers with low density (probably less than 0.1 per Cu). Remembering the discussion on the susceptibility data, the carriers with such low density are assigned to the holes in the ladders. The study of optical conductivity spectrum has revealed that the holes are transferred from chains to ladders upon Ca substitution.¹⁹ From the conductivity sum (spectral weight) transferred hole density δ (per ladder-Cu) has been estimated at each x . δ increases from 0.07 at $x = 0$ to 0.20 at $x = 11$. At the expense of the increases in ladder holes, the chain-hole density δ' , which is assumed to be $\delta' \sim 0.5$ (per chain-Cu) at $x = 0$, decreases to $\delta' \sim 0.32$ at $x = 11$. The decrease in δ' with x exactly follows the x dependence of N_{spin} shown in the inset of Fig. 1(b).

As regards the electronic anisotropy of $\text{Sr}_3\text{Ca}_{11}\text{Cu}_{24}\text{O}_{41}$, a contrasting behavior is seen in the resistivity. The T dependences of resistivity for $\text{Sr}_3\text{Ca}_{11}\text{Cu}_{24}\text{O}_{41}$ are shown in Fig. 3 in all three directions. ρ_a , i.e., interladder resistivity, is by 15 to 40 times higher than ρ_c and the resistivity in the b direction (ρ_b) (perpendicular to the ladder planes) is higher than ρ_a by two orders. Although at low temperatures, below ~ 50 K, the resistivity goes up in any direction, a metallic behavior characterized by nearly T -linear dependence is seen in ρ_c above 80 K. The T dependence of ρ_a is anomalous in that $d\rho_a/dT$ is negative

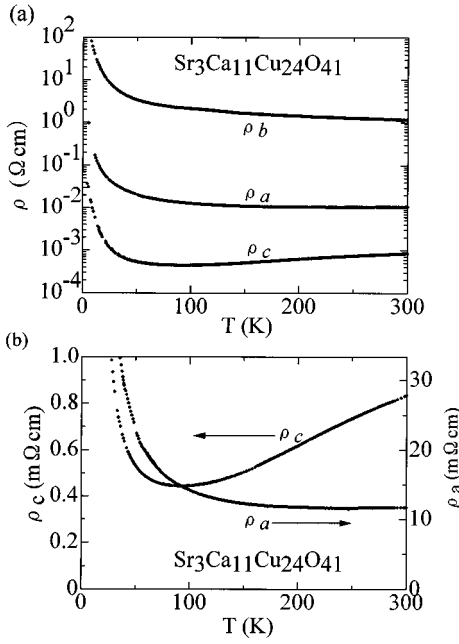


FIG. 3. The temperature dependence of the resistivity for the most conductive compound, $\text{Sr}_3\text{Ca}_{11}\text{Cu}_{24}\text{O}_{41}$ along the three principal axes. The c - and a -axis resistivity are shown in the lower panel on the linear scale.

(i.e., insulating) in the temperature range where $d\rho_c/dT$ is positive (metallic).²⁰ Such a contrasting T dependence between ρ_c and ρ_a is analogous to that observed between the in-plane (ρ_{ab}) and out-of-plane (ρ_c) resistivity in the underdoped high- T_c cuprates.²¹ Extending the discussion by Anderson and Zou²² to the present case, the T dependence of ρ_a gives evidence that the electronic state in the present system is one-dimensional, that is, holes are confined within ladders. In the case of underdoped high- T_c cuprates, the confinement of the carriers within the Cu-O planes appears to be related to the presence of a spin gap.²³ The presence of a spin gap in the ladders is confirmed for $\text{Sr}_{14}\text{Cu}_{24}\text{O}_{41}$ by NMR measurements,^{24,25} but the gap width seems to rapidly shrink with increase of Ca content. In the hole-doped ladders the spin gap is related to the formation of a hole pair (or a bipolaron) between two holes on the same rung.²⁶ The hole pairs are presumably unable to hop between ladders, and a finite energy is necessary for the holes to hop by breaking the pairs.

As a sign of superconductivity has been reported on the compound with $x = 13.6$ under high pressure of about 3 GPa,⁴ it is interesting to see the effect of pressure on the resistivity and its anisotropy. The T dependences of ρ_c and ρ_a for the $x = 11$ crystal are shown in Fig. 4 at ambient pressure and at 2 GPa. The pressure effect is not large but a significant change is seen in the metallic region of ρ_c . ρ_c decreases by $\sim 20\%$ at $T = 300$ K under 2 GPa, but it is nearly pressure independent at $T \sim 100$ K where ρ_c shows a minimum. This implies that the slope of ρ_c - T characteristics decreases with pressure which results, if not all, from an increase in the ladder hole density. Plausibly, the pressure would have a similar effect to the Ca substitution which corresponds to an application of chemical pressure because of the smaller ionic radius of Ca. At low temperatures ρ_c

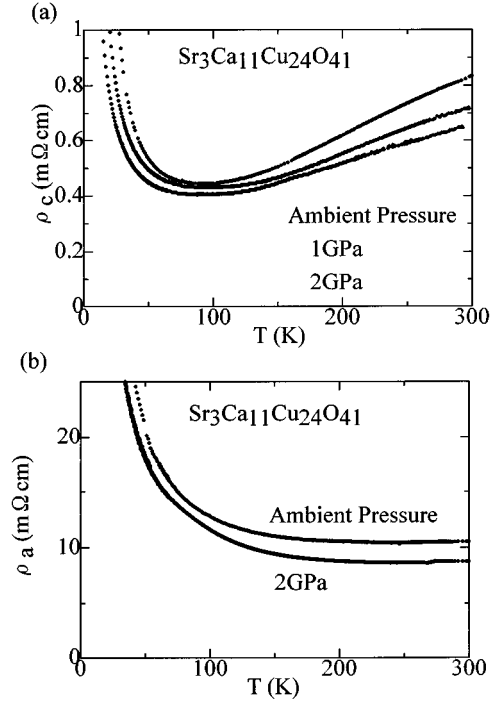


FIG. 4. The temperature dependence of the resistivity under 0–2 GPa for $\text{Sr}_3\text{Ca}_{11}\text{Cu}_{24}\text{O}_{41}$ along the (a) c and (b) a axis.

becomes insensitive to pressure. The residual resistivity ($\sim 400 \mu\Omega \text{ cm}$) is fairly large which may be a reason for carrier localization as discussed below.

The T dependence of the interladder resistivity ρ_a is not essentially changed under pressure. The T coefficient of ρ_a remains negative over the T range below 300 K but the magnitude of ρ_a decreases by about 20% at 2 GPa, nearly the same as that of ρ_c at $T = 300$ K. The anisotropic ratio ρ_a/ρ_c at 2 GPa is nearly the same as that at ambient pressure. In this respect, the pressure never changes the electronic state of the hole-doped ladders.

Finally, we discuss the nature of localization of carriers based on the result on the $x = 11$ crystal. A ‘‘classical’’ Mott-Ioffe-Regel criterion for metallic conductivity is given by

$$\rho^* \sim (h/e^2)(\pi/c)ab \sim 0.9 \text{ m}\Omega \text{ cm} \quad (1)$$

for a quasi-1D electric system with an open Fermi surface along the c axis. Here, a , b , and c are the spacing between neighboring ladders, the spacing between the ladder plane, and the lattice constant along the ladder, respectively. The value of $\rho_c \sim 0.4 \text{ m}\Omega \text{ cm}$, for $x = 11$ is well below ρ^* . Nevertheless, the carriers are localized at low temperatures.

A possible resolution for this controversy is to suppose that the ladder plane (ac plane) is an anisotropic 2D system for a single hole. In this case the Mott-Ioffe-Regel criterion is

$$\rho_{2D}^* \sim (h/e^2)b \sim 1.7 \text{ m}\Omega \text{ cm}. \quad (2)$$

The observed values of ρ_c and ρ_a yield $\sqrt{\rho_a\rho_c} \sim 2.5 \text{ m}\Omega \text{ cm} > \rho_{2D}^*$ consistent with the observed localization. An alternative resolution is to assume that the holes form pairs within a ladder and the hole pairs are local-

ized. In this case e should be replaced by $2e$ in ρ^* , yielding $\rho^* \sim 0.2 \text{ m}\Omega \text{ cm}$ well below the observed ρ_c . At present it is not certain whether ρ_c (or $\sqrt{\rho_a \rho_c}$) becomes smaller than ρ^* (or ρ_{2D}^*), when we increase the Ca content to $x = 13.6$ and apply pressure up to 3 GPa, the conditions Uehara *et al.* reported for superconducting transition at $T_c \sim 12 \text{ K}$.⁴ From the present result together with the result of the optical experiment,¹⁹ we can estimate the hole density in the ladders as $\delta \sim 0.3$ for $x = 13.6$ at 3 GPa.

In summary, we have presented the data of anisotropic electric resistivity and magnetic susceptibility of single crystals of the $\text{Sr}_{14}\text{Cu}_{24}\text{O}_{41}$ system. The two-leg Cu_2O_3 ladders contained in this material are progressively doped with holes upon Ca substitution and upon applying hydrostatic pressure. The electric properties are thus determined by the hole-

doped ladders, whereas the magnetic properties are dominated by the contribution from CuO_2 chains which also have a role as a charge reservoir.

A remarkable anisotropy in resistivity gives evidence for one-dimensional charge transport in the ladders. The one-dimensionality is not essentially changed by applied pressure.

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- ¹J. G. Bednorz and K. A. Müller, *Z. Phys. B* **64**, 189 (1986).
²T. M. Rice, S. Gopalan, and M. Sigrist, *Europhys. Lett.* **23**, 445 (1993).
³E. Dagotto, J. Riera, and D. Scalapino, *Phys. Rev. B* **45**, 5744 (1992).
⁴M. Uehara *et al.*, *J. Phys. Soc. Jpn.* **65**, 2764 (1996). These authors have recently reported superconductivity in $\text{Sr}_{0.4}\text{Ca}_{13.6}\text{Cu}_{24}\text{O}_{41}$ with $T_c = 12 \text{ K}$ under high pressures.
⁵Z. Hiroi *et al.*, *J. Solid State Chem.* **95**, 230 (1995).
⁶Z. Hiroi and M. Takano, *Nature (London)* **377**, 41 (1995).
⁷M. W. McElfresh *et al.*, *Phys. Rev. B* **40**, 825 (1989).
⁸M. Kato, K. Shiota, and Y. Koike, *Physica C* **258**, 284 (1996).
⁹M. Uehara, M. Ogawa, and J. Akimitsu, *Physica C* **255**, 193 (1995).
¹⁰S. A. Carter, *et al.*, *Phys. Rev. Lett.* **77**, 1378 (1996).
¹¹M. Matsuda and K. Katsumata, *Phys. Rev. B* **53**, 12 201 (1996).
¹²M. Matsuda *et al.*, *Phys. Rev. B* **54**, 12 199 (1996).
¹³J. Akimitsu *et al.*, *Physica C* **263**, 475 (1996).
¹⁴E. M. McCarron *et al.*, *Mater. Res. Bull.* **23**, 1355 (1988).
¹⁵T. Siegrist *et al.*, *Mater. Res. Bull.* **23**, 1429 (1988).
¹⁶I. Tanaka and H. Kojima, *Nature (London)* **337**, 21 (1989).
¹⁷M. Troyer, H. Tsunetsugu, and D. Würtz, *Phys. Rev. B* **50**, 13 515 (1994).
¹⁸N. Motoyama, H. Eisaki, and S. Uchida, *Phys. Rev. Lett.* **76**, 3212 (1996).
¹⁹T. Osafune, N. Motoyama, H. Eisaki, and S. Uchida (unpublished).
²⁰Note that the magnitude of the anisotropy ρ_a/ρ_c is relatively small as compared with the corresponding ratio ρ_c/ρ_{ab} in high- T_c cuprates which ranges from 30 to more than 10^4 . The complicated T dependence of resistivity observed for randomly oriented crystals (Refs. 4 and 9) is ascribable to the contrasting T dependence of ρ_c and ρ_a in spite of rather small anisotropy.
²¹T. Ito *et al.*, *Nature (London)* **350**, 596 (1991).
²²P. W. Anderson and Z. Zou, *Phys. Rev. Lett.* **60**, 132 (1988).
²³B. Batlogg and V. J. Emery, *Nature (London)* **382**, 20 (1996).
²⁴S. Matsumoto *et al.* (unpublished).
²⁵S. Tsuji, K. Kumagai, M. Kato, and Y. Koike, *J. Phys. Soc. Jpn.* **63**, 42 (1996).
²⁶H. Tsunetsugu, M. Troyer, and T. M. Rice, *Phys. Rev. B* **49**, 16 078 (1994); **51**, 16 456 (1995).